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14. ABSTRACT

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AN AUTOMATED PROCESS FOR GENERATION OF NEW FUEL BREAKDOWN MECHANISMS

(Grant/Contract Number FA9550-06-1-0376)

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SUMMARY/OVERVIEW

Practical fuels, such as JP8, derived from the refinery processing of crude petroleum, are chemically complex, often containing thousands of compounds. Because these fuels need to meet broadly defined specifications, their compositions vary not only with refinery and crude oil source, but also with season and year of production. As a result, it is difficult to control the consistency in fuel composition required for the purpose of research. When dealing with these complex fuels, surrogates, mixtures of a limited number of hydrocarbons with a well-defined and reproducible composition, can be used in place of the real fuel both for experimental and computational applications.

The work performed by our research group over the last years aimed to develop an integrated and innovative computational approach for predicting reaction mechanisms for JP8 surrogate components. The modeling effort has integrated various computational tools to build chemical kinetic pathways, starting from the structure of the proposed fuel components and ending with a list of reactions pathways, rate constants, thermodynamic and transport data.

Studies were conducted in several research areas, all of which were directed at meeting the overall project objectives. The chemistry of H abstraction reactions from various hydrocarbons was obtained using *ab initio* methods. Reaction class theory was applied to extend the knowledge obtained with quantum chemistry methods to large classes of reactions. Transport properties of n-alkane were determined using molecular dynamics simulations in conjunction with the Green-Kubo theory. The results have been integrated in the first generation of a jet fuel mechanism.

TECHNICAL DISCUSSION

The innovative aspect of the modeling effort carried out over the last years has been the integration of computational tools to build reaction mechanisms for real fuel mechanisms, including chemical pathways, rate constants, and transport data. The results described below are organized in two main areas: kinetics and transport properties of JP8 surrogate components.

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1. H abstraction reactions: *ab initio* simulations and Transition State Theory

Hydrogen abstraction reactions are an important part of the kinetic mechanisms available in the literature to study combustion systems. We, therefore, focused our effort on obtaining accurate rate constants for various hydrocarbons using multiple radicals, such as H, OH, CH_3, and O, as incoming species for the abstraction. The discussion below summarizes the results obtained for alkene compounds.

The hydrogen abstraction reaction between a hydroxyl radical (OH) and an alkene (C=C) to form a water molecule (H_2O) and an alkenyl radical (C=C•) is known to be an important reaction class in combustion processes of hydrocarbon fuel, especially in the high temperature regime. The hydrogen abstraction reaction between C_2H_4 and OH to form C_2H_3 and H_2O has attracted a number of extensive experimental, as well as theoretical, investigations. There are more than 15 entries for rate constant studies for this reaction in the NIST chemical kinetics database. For reactions involving alkenes larger than C_2H_4, even fewer data are available due to the involvement of other kinds of reactions such as the addition of OH to the double bond and the hydrogen abstraction at different carbon sites, e.g. saturated carbon sites (sp^3 hybridization).

All the electronic structure calculations were carried out using the GAUSSIAN 03 program. Hybrid non-local Density Functional Theory (DFT), particularly Becke's half-and-half (BH&H) non-local exchange and Lee-Yang-Parr (LYP) non-local correlation functionals, has been found to be sufficiently accurate for predicting the transition state properties, e.g. barrier height and vibrational frequency, for hydrogen abstraction reactions by a radical. Geometries of reactants, transition states, and products were optimized at BH&HLYP level of theory with the Dunning's correlation-consistent polarized valence triple-zeta basis set, denoted as cc-pVTZ, that is sufficient to capture the physical change along the reaction coordinate for this type of reaction. Frequencies of the stationary points were also calculated at the same level of theory. This information was used to derive the RC-TST factors described in the following section. Thermal rate constants were computed for the temperature range of 300-3000 K. The correction for the hindered rotors, e.g. reduced moment of inertia and the periodic potential, are then obtained using the information on the rate constants.

Figure 1 reports the rate constants available in the literature for this reaction obtained by experiments and simulations. Tully et al. [1] used the laser photolysis/laser-induced fluorescence technique under slow-flow conditions to measure the rate constants in the temperature range of 650-901 K. Baulch et al. [2] presented critically evaluated kinetic data for use in computer combustion modeling. The suggested rate data with an uncertainty factor of 3 in the temperature range of 650-1500 K follow closely the studies of Tully et al. [1] Westbrook et al. [3] suggested rate constant data for the reference reaction in the temperature range 1003-1253 K. Using visible-UV absorption technique together with TST model, Liu et al. [4] reported the rates of the hydrogen abstraction in the temperature range of 723 - 1170 K. With the energetic data obtained at the QCISD(T)/6-311G(2df,p)//B3LYP/6-31G(d,p) together with the gradient and Hessian information at the B3LYP/6-31G(d,p), Liu et al.[5] reported thermal rate constants in the temperature range of 200-5000 K using the canonical variational transition state theory (CVT) and the small-curvature tunneling correction (SCT). Recently, Senosiain et al.[6] also carried out an analysis of the $OH+C_2H_4 \rightarrow H_2O+C_2H_3$ reaction using the CVT method with the molecular-property data obtained at the RQCISD(T)/cc-pV∞Z//UB3LYP/6-311++G(d,p) level of theory

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to suggest rate constants for this reaction. The two rate constants obtained with the CVT theory are similar (within a deviation factor of 4) in the high temperature regime but they differ by an order of magnitude at lower temperature (< 500 K).
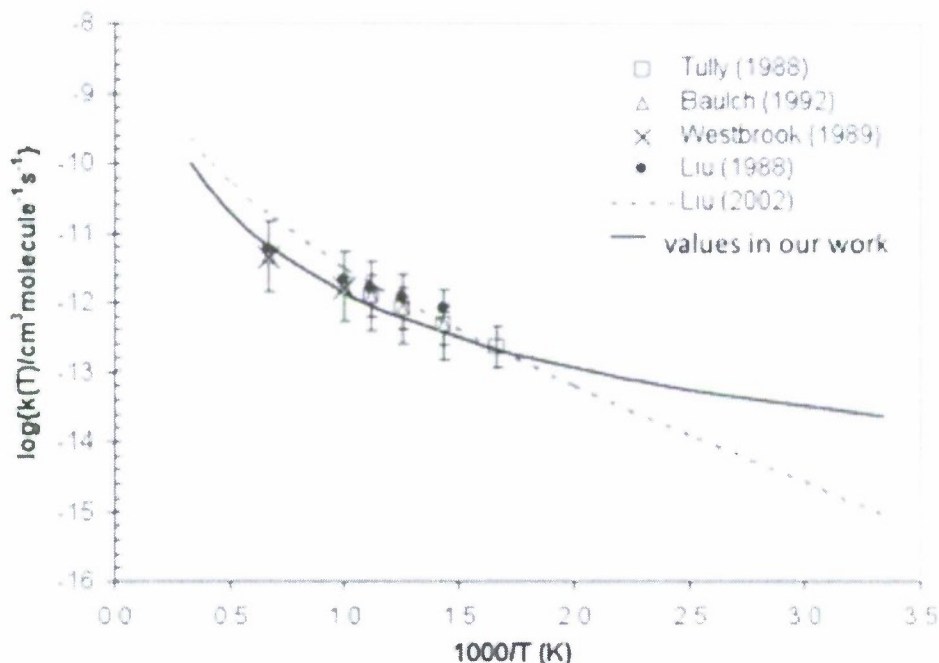

Figure 1: Arrhenius plots of rate constants for the reaction OH+C_2H_4 → H_2O+C_2H_3. The error bars for these rate constants are also included.

The rate constant derived in our study for the reaction OH + C_2H_4 → H_2O + C_2H_3 has the following expression:

$$k_r(T) = 2.18 \times 10^{-25} \times T^{4.20} \times \exp\left[\frac{433}{T}\right], \text{ [cm}^3\text{molecule}^{-1}\text{s}^{-1}]$$
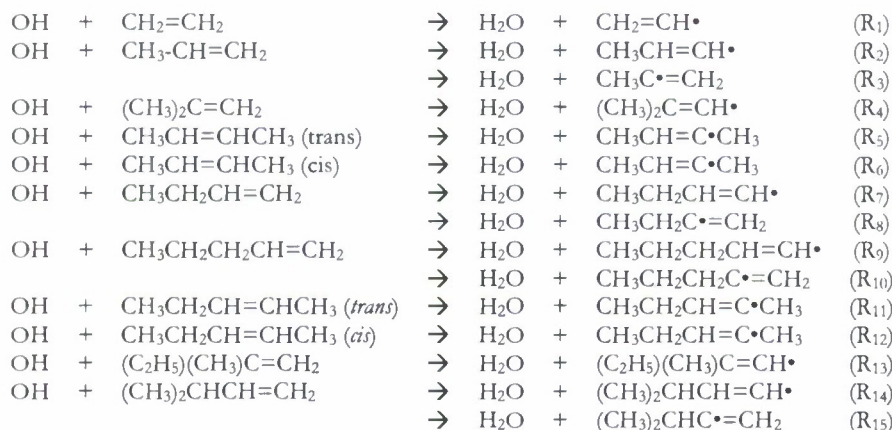
In a similar way, we determined rate constants for H abstraction reactions from other key reactions, including aromatics containing 5 and 6-member rings.

2. Reaction Class Theory for classes of hydrocarbons

Detailed chemical kinetic descriptions of real fuel combustion require the tracking of hundreds of chemical species and thousands of reaction steps. It is impracticable to obtain the correct kinetic data for such a large number of reactions by experiments or explicit rate-constant calculations even using the simple Transition State Theory method. To this end, studies were conducted by our research group using the Reaction Class Transition State Theory for estimating rate constants of a large number of reactions. As an example, below we report the results obtained for the OH+alkene reaction class. The main task was to find correlation expressions between rate

constants of the reference reaction (C_2H_4 + OH = C_2H_3 + H_2O) and those of other reactions in the class (C_nH_{2n} + OH) from explicit direct *ab initio* dynamics calculations of the rate constants of a representative set in the class itself.

To compute the Reaction Class Transition State Theory (RC-TST) parameters for the OH+alkene class, 15 reactions are considered as a representative set. These reactions are given below:

OH	+	$CH_2=CH_2$	→	H_2O	+	$CH_2=CH\bullet$	(R_1)
OH	+	CH_3-$CH=CH_2$	→	H_2O	+	$CH_3CH=CH\bullet$	(R_2)
			→	H_2O	+	$CH_3C\bullet=CH_2$	(R_3)
OH	+	$(CH_3)_2C=CH_2$	→	H_2O	+	$(CH_3)_2C=CH\bullet$	(R_4)
OH	+	$CH_3CH=CHCH_3$ (trans)	→	H_2O	+	$CH_3CH=C\bullet CH_3$	(R_5)
OH	+	$CH_3CH=CHCH_3$ (cis)	→	H_2O	+	$CH_3CH=C\bullet CH_3$	(R_6)
OH	+	$CH_3CH_2CH=CH_2$	→	H_2O	+	$CH_3CH_2CH=CH\bullet$	(R_7)
			→	H_2O	+	$CH_3CH_2C\bullet=CH_2$	(R_8)
OH	+	$CH_3CH_2CH_2CH=CH_2$	→	H_2O	+	$CH_3CH_2CH_2CH=CH\bullet$	(R_9)
			→	H_2O	+	$CH_3CH_2CH_2C\bullet=CH_2$	(R_{10})
OH	+	$CH_3CH_2CH=CHCH_3$ (*trans*)	→	H_2O	+	$CH_3CH_2CH=C\bullet CH_3$	(R_{11})
OH	+	$CH_3CH_2CH=CHCH_3$ (*cis*)	→	H_2O	+	$CH_3CH_2CH=C\bullet CH_3$	(R_{12})
OH	+	$(C_2H_5)(CH_3)C=CH_2$	→	H_2O	+	$(C_2H_5)(CH_3)C=CH\bullet$	(R_{13})
OH	+	$(CH_3)_2CHCH=CH_2$	→	H_2O	+	$(CH_3)_2CHCH=CH\bullet$	(R_{14})
			→	H_2O	+	$(CH_3)_2CHC\bullet=CH_2$	(R_{15})

where *trans* and *cis* denote trans- and cis- configurations for the carbon chain. Note that this set does not include reactions with resonance systems, e.g. 1,3-butadiene, as well as aromatic systems, e.g. benzene.

The basic idea of the RC-TST technique is that reactions belonging to a specific class have the same reactive moiety; thus the difference between the rate constants of any two reactions in the class is mainly due to the difference in the interactions between the reactive moiety and their different substituents. Within the RC-TST framework, the rate constants of an arbitrary reaction (denoted as k_a) are proportional to those of a reference reaction, k_r (usually the smallest reaction in the class, which is referred to as the principal reaction) in the same class by a temperature dependent function $f(T)$:

$$k_a(T) = f(T) \times k_r(T) \tag{1}$$

The rate constants for the reference reaction are often known experimentally or can be calculated accurately from first-principles. The key idea of the RC-TST method is to factor $f(T)$ into different components under the TST framework:

$$f(T) = f_\sigma \times f_\kappa \times f_Q \times f_V \tag{2}$$

where f_σ, f_κ, f_Q and f_V are the symmetry number, tunneling, partition function and potential energy factors, respectively. These terms are simply the ratios of the corresponding components in the TST expression for the arbitrary and reference reactions:

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$$f_\sigma = \frac{\sigma_a}{\sigma_r} \tag{3}$$

$$f_\kappa(T) = \frac{\kappa_a(T)}{\kappa_r(T)} \tag{4}$$

$$f_Q(T) = \frac{\left(\dfrac{Q_a^\ddagger(T)}{\Phi_a^R(T)}\right)}{\left(\dfrac{Q_r^\ddagger(T)}{\Phi_r^R(T)}\right)} = \frac{\left(\dfrac{Q_a^\ddagger(T)}{Q_r^\ddagger(T)}\right)}{\left(\dfrac{\Phi_a^R(T)}{\Phi_r^R(T)}\right)} \tag{5}$$

$$f_V(T) = \exp\left[-\frac{(\Delta V_a^\ddagger - \Delta V_r^\ddagger)}{k_B T}\right] = \exp\left[-\frac{\Delta\Delta V^\ddagger}{k_B T}\right] \tag{6}$$

where σ is the reaction symmetry number; $\kappa(T)$ is the transmission coefficient accounting for the quantum mechanical tunneling effects; $Q^\ddagger$ and Φ^R are the total partition functions (per unit volume) of the transition state and reactants; $\Delta V^\ddagger$ is the classical reaction barrier height; T is the temperature in Kelvin; k_B and h are the Boltzmann and Planck constants, respectively. The potential energy factor can be calculated using the reaction barrier heights of the arbitrary reaction and the reference reaction. The classical reaction barrier height $\Delta V^\ddagger$ for the arbitrary reaction can be obtained using the Linear Energy Relationship (LER), similar to the well-known Evans-Polanyi linear free energy relationship,[7-9] between classical barrier heights and reaction energies in a given class without having to calculate them explicitly. Alternatively, the barrier height for the arbitrary reaction can be obtained from the Barrier Height Group (BHG) approach where reactions in a sub-class can be reasonably assumed to have the same barrier height.

The potential energy factor can be calculated using Eq. (6), where $\Delta V_a^\ddagger$ and $\Delta V_r^\ddagger$ are the barrier heights of the arbitrary and reference reactions, respectively. We have also shown that within a given class there is a linear energy relationship (LER) between the barrier height and the reaction energy, similar to the well-known Evans-Polanyi linear free energy relationship. Thus, accurate barrier heights can be predicted from only the reaction energies. The barrier heights for reactions R_1-R_{15} can also be grouped into two classes: terminal carbon sites of the double bond (*class 1*) and non-terminal carbon sites (*class 2*). This can be referred to as the barrier height grouping (BHG). The AM1 semi-empirical method was employed to calculate the reaction energies. AM1 and BH&HLYP/cc-pVTZ reaction energies were then used to derive the LER's between the barrier heights and reaction energies.

The observed LERs plotted against the reaction energies calculated at BH&HLYP/cc-pVTZ and AM1 levels are shown in Figs. 2a and 2b, respectively. The substitute of an alkyl group will stabilize the radical products thus lowering the barrier heights. For this reason the reactions at the non-terminal carbon of the double bond (*class 2*) have barrier heights of about 2.0 kcal/mol lower than those at the terminal sites.

The linear fits for these reactions were obtained using the least square fitting method and have the following expressions:

$$\Delta V^* = 0.4892 \times \Delta E^{BH\&HLYP} + 10.772 \quad (\text{kcal/mol}) \tag{8a}$$

$$\Delta V^* = 0.4238 \times \Delta E^{AM1} + 16.572 \qquad\qquad (\text{kcal/mol}) \tag{8b}$$

Based on the BHG results, we assigned the values of 10.50 and 8.27 kcal/mol to the energy barriers of the terminal and non-terminal carbon sites of the double bond, respectively. It is interesting to note that the averaged deviations of reaction barrier heights estimated from the BHG (0.15 kcal/mol) is smaller than that of the LER, while the maximum deviation (0.46 kcal/mol) is higher. Therefore, this approach can be used to estimate the relative barrier height quickly with an acceptable confidence. The key advantage of this approach is that it does not require any additional information to estimate rate constants.

In conclusion, the barrier height of any reaction in the OH+alkene reaction class can be obtained by using either the LER or BHG approach. The estimated barrier height is then used to calculate the potential energy factor using Eq. (6). The performance of both approaches is discussed in the error analyses below.
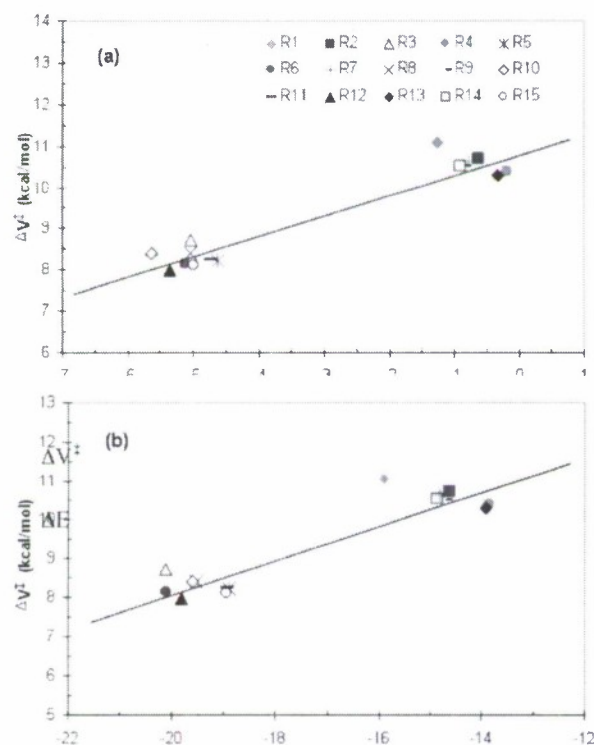

Figure 2: Linear energy relationship plots of the barrier heights versus the reaction energies, computed at (a) BH&HLYP/cc-pVTZ and (b) AM1 levels of theory.

The tunneling factor f_κ is the ratio of the transmission coefficient of reaction R_a to that of reaction R_r. Due to the cancellation of errors in evaluating the tunneling factors, we have shown that the factor f_κ can be reasonably estimated using the one-dimension Eckart method. In the Eckart formulation, the imaginary frequency and the barrier height are used to calculate the tunneling probability for a reaction. Because the barrier heights are grouped into 2 classes, namely terminal and non-terminal sites of the double-bond carbon and the imaginary frequencies for reactions at the same class are very similar, the values of the tunneling coefficients for reactions in the same class are expected to be similar. Therefore, the average value for the tunneling factors can be used for the whole group. Simple expressions for the two tunneling factors for terminal and non-terminal carbon sites of the double bond are obtained by fitting to the average calculated values and are given below:

$$f_\kappa = 0.999 - 83.42 \times \exp[-0.51 \times T^{0.42}] \qquad \text{for terminal carbon sites} \tag{9a}$$

$$f_\kappa = 0.978 - 7.55 \times \exp[-0.056 \times T^{0.66}] \qquad \text{for non-terminal carbon sites} \tag{9b}$$

The correlation coefficients for these fits are larger than 0.999. The same tunneling factor expression can be reasonably assigned to different reactions in the same class with the largest

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unsigned deviation of 0.08 for R_{13} and the largest percentage deviation of 17.2%. The mean unsigned deviation is 7%, compared to the direct Eckart calculation using reaction information from BH&HLYP/cc-pVTZ level of theory. At higher temperatures, tunneling contributions to the rate constants decrease and thus, as expected, the differences between the approximated values and the explicitly calculated ones also decrease; for example, the maximum error for all reactions is less than 2% at 500 K.

The partition factor includes translational, rotational, internally-rotational, vibrational, and electronic components. The partition function factor f_Q mainly originates from the differences in the coupling between the substituents and the reactive moiety. Its temperature dependence arises from the vibrational and internally-rotational components only.

The averaged values of partition function factors for reactions R_2-R_{15} are fitted into the following analytical expression:

$$f_Q = 0.71 - 2.08 \times \exp[-0.18 \times T^{0.45}] \tag{10}$$

The coupling between subtituents with the reactive moiety is believed to account for the partition function factors having values of around 0.7. The total coupling effect is contributed from those of the translational, rotational and vibrational partition function factors. Each reaction class has a specific coupling effect mainly due to the specific/unique reactive moiety. If there is no coupling effect, the values of the partition function factors would be expected to be very close to unity.

For this reaction class, the rotation of the alkyl group (CH_3) along the C—C bond at some reactants, transition states and products as well as the rotation of the hydroxyl (OH) group along the C—O axis at all transition states need to be treated as hindered rotations. The hindered rotation treatment lowers the total rate constants with the temperature increase. Note that the principal reaction R_1 does not have the internal rotation of the CH_3 group. The averaged values, as applied to the whole class, are fitted into an analytical expression as given below:

$$f_{HR} = 1.01 - 0.72 \times \exp[-1332 \times T^{-0.99}] \tag{11}$$

So far we have established the necessary parameters - namely the potential energy, the symmetry number, the tunneling and the partition function factors - for application of the RC-TST theory to predict rate constants for reactions in the OH+Alkene class.

The procedure for calculating the rate constants of an arbitrary reaction in this class is: a) calculate the potential energy factor using Eq. (6) with the $\Delta V_r^{\ddagger}$ value of 11.07 kcal/mol. The reaction barrier height can be obtained using the LER approach by employing Eq. (8a) for BH&HLYP/cc-pVTZ reaction energies or (8b) for AM1 reaction energies or by the BHG approach; (b) calculate the symmetry number factor from Eq. (3) or see Table 2; (c) compute the tunneling factor using Eq. (9a) and (9b) for terminal and non-terminal carbon sites, respectively; (d) evaluate the partition function factor using Eq. (10) with the hindered roration treatment correction using Eq. (11); and (e) the rate constants of the arbitrary reaction can be calculated by taking the product of the reference reaction rate constants given by Eq. (7) with the reaction class factors.

Table 2 summarizes the RC-TST parameters for this reaction class. If the BHG barrier heights and the average values for the factors are used, the rate constants are denoted by RC-TST/BHG. The RC-TST/BHG rate constants for any reaction belonging to this reaction class are:

$$k(T) = 7.51 \times 10^{-24} \times T^{3.59} \times \exp\left[\frac{185}{T}\right] \text{ for terminal carbon sites} \qquad (12a)$$

$$k(T) = 1.00 \times 10^{-22} \times T^{3.19} \times \exp\left[\frac{763}{T}\right] \text{ for non-terminal carbon sites} \qquad (12b)$$

Because the terminal carbon sites have two hydrogen atoms which can be reasonably considered equivalent in some cases, and the non-terminal sites only have one hydrogen atom, the symmetry factors of 2 and 1 are also included in the rate constant expressions.

TABLE 2: Parameters and Formulations of the RC-TST Method for the OH + Alkene → H$_2$O + Alkenyl Reaction Class (OH+ C$_2$H$_4$ is the reference reaction)

$$k(T) = f_\sigma \times f_\kappa(T) \times f_Q(T) \times f_{HR}(T) \times f_v(T) \times k_r(T) \,;\, f_v(T) = \exp\left[\frac{-(\Delta V^\ddagger - \Delta V_r^\ddagger)}{k_B T}\right]$$

T is in Kelvin; $\Delta V^\ddagger$ and ΔE are in kcal/mol; Zero-point energy correction is not included

f_σ	Calculated explicitly from the symmetry of reactions (see Table 2)
$f_\kappa(T)$	$f_\kappa = 0.999 - 83.42 \times \exp[-0.51 \times T^{0.42}]$ for terminal carbon sites. $f_\kappa = 0.978 - 7.55 \times \exp[-0.056 \times T^{0.66}]$ for non-terminal carbon sites.
$f_Q(T)$	$f_Q = 0.71 - 2.08 \times \exp[-0.18 \times T^{0.45}]$
$f_{HR}(T)$	$f_{HR} = 1.01 - 0.72 \times \exp[-1332 \times T^{-0.99}]$
$\Delta V^\ddagger$	LER $\quad \Delta V^\ddagger = 0.4892 \times \Delta E^{BH\&HLYP} + 10.772$ $\quad\quad\quad \Delta V^\ddagger = 0.4238 \times \Delta E^{AM1} + 16.572$ $\Delta V_r^\ddagger = -11.07$ kcal/mol [a]
$k_r(T)$ (Eq.7)	$k_r(T) = 2.18 \times 10^{-25} \times T^{4.20} \times \exp\left[\frac{433}{T}\right]$, [cm^{3}molecule^{-1}s^{-1}]

To illustrate the theory we selected two reactions R_2 and R_3 whose rate constants are available in the literature.

Figs. 3a~b show the predicted rate constants of reaction R_2 and reaction R_3 using the RC-TST method. Since the barrier heights obtained from either BH&HLYP/cc-pVTZ or AM1 energies are similar, we can expect their rate constants to be similar.

The rate constants estimated from the RC-TST/LER and RC-TST/BHG approaches are comparable for reactions R_2 and R_3 due to the similar predicted values of the barrier heights, e.g. 10.47 and 10.50 kcal/mol for R_2 from LER and BHG, respectively. The difference in rate constants might be larger for other reactions.

Compared to the "RC-TST exact" values, the excellent performance of the RC-TST for these two reactions can be seen in Figure 3.
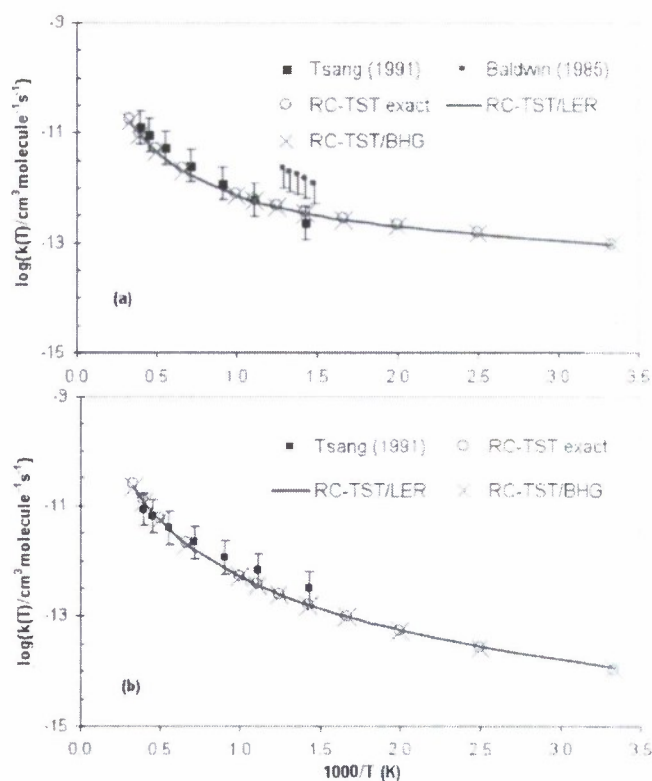

Figure 3: Arrhenius plots of the calculated rate constants using the RC-TST method for two representative hydrogen abstraction reactions along with the available values: (a) OH+C3H6 at the terminal carbon, and (b) OH+C3H6 at the non-terminal carbon.

3. Diffusion Coefficients of Fuel Surrogate Components using Molecular Dynamics Simulations

In solving chemically reacting-flow problems, however, chemical production and destruction is often balanced by transport due to convection, diffusion, or conduction and, hence, accurate transport coefficients are of great importance in the development of reaction mechanisms. Therefore, in addition to kinetic studies, we have initiated an analysis of the transport properties of hydrocarbons using Molecular Dynamics simulations. Specifically, we have looked at the binary diffusion coefficients of n-alkane molecules.

The Chapman Enskog (CE) relationship is the theoretical equation currently used to compute the diffusion coefficients of different systems.[10, 11] Combined with the Lennard-Jones intermolecular potential function, the binary diffusion coefficient can be expressed as:

$$D_{12} = \frac{3}{16} \frac{\sqrt{2\pi(k_B T)^3 / m_{12}}}{P\pi\sigma_{12}^2 \Omega}$$

where k_B is the Boltzmann constant and m_{12} is the reduced mass of the pair components. This expression contains a dependence on the temperature, T, pressure, P, the average collision diameter between two species, σ_{12}, and the collision integral, Ω. The collision integral term is related to the interaction energy of two molecules and the scattering phenomena when the collision.[12] The value of the collision integral depends on the reduced temperature, $T^* = {k_B T}/{\varepsilon_{12}}$, where ε_{12} is the well depth of the Lennard-Jones energy potential.

This approach presents many limitations. The CE equation considers the gases as hard spheres and requires accurate values of the collision diameter and potential energy well depth. These parameters are usually not available and in many cases they are assumed based on similarity.

The CE equation does not give reliable transport data under high density or high temperature conditions especially for binary diffusion case. The Chapman-Enskog equation is valid only for $\rho^* < 0.1$ where

$$\rho^* = \rho \sigma_e^3$$

ρ is the number density of the system and σ_e is the effective hard sphere diameter which depends on temperature.[13]

Finally, the CE equation does not take into account the effect of molecular geometry variations on the mutual diffusion coefficient of isomers, an important factor especially in high density or high mobility conditions.

The Green-Kubo relations provide the exact mathematical expression for transport coefficients in terms of microscopic fluctuations of the system of interest.[14] For the self diffusion coefficient, the Green Kubo is the time integral of the velocity auto-correlation function, which represents the correlation between molecules at different times[15]

$$D_1 = \frac{1}{3N_1} \sum_{i=1}^{N_1} \int_0^\infty \left\langle \vec{u}_i(t) \cdot \vec{u}_i(0) \right\rangle dt$$

where N_1 is the total number of particles of species 1, $\vec{u}_i$ is the velocity component of particle i of species 1, and the angular brackets denote the ensemble average of velocity auto correlation functions. The binary diffusion coefficient can be expressed as the combination of the time integral of the velocity auto- and cross-correlation function, which is the correlation between the different molecules at different times.

$$D_{12} = Q \left[x_2 D_1 + x_1 D_2 + x_1 x_2 \left(\frac{f_{11}}{x_1^2} + \frac{f_{22}}{x_2^2} - 2 \frac{f_{12}}{x_1 x_2} \right) \right]$$

$$f_{\alpha\beta} = \frac{1}{3N} \sum_{i=1}^{N_\alpha} \sum_{j \neq i}^{N_\beta} \int_0^\infty \left\langle \vec{u}_i(t) \cdot \vec{u}_j(0) \right\rangle dt$$

where Q is the thermodynamic factor determined from the integral of the radial distribution functions with respect to the ensemble.[16] x_1 and x_2 are the mole fractions of the species 1 and 2;

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D_1 and D_2 are the self diffusion coefficients of the species 1 and 2 in the mixture; $f_{\alpha\beta}$ is the ensemble average of the time integral of the velocity cross-correlation function.

Molecular Dynamics simulations have been used to derive the microscopic information in terms of the time integral of the velocity cross-correlation components of the species in various temperature and pressure regimes. As initial ensemble, we studied n-alkane compounds with the goal to determine the accuracy of C-E in dealing with long molecules.
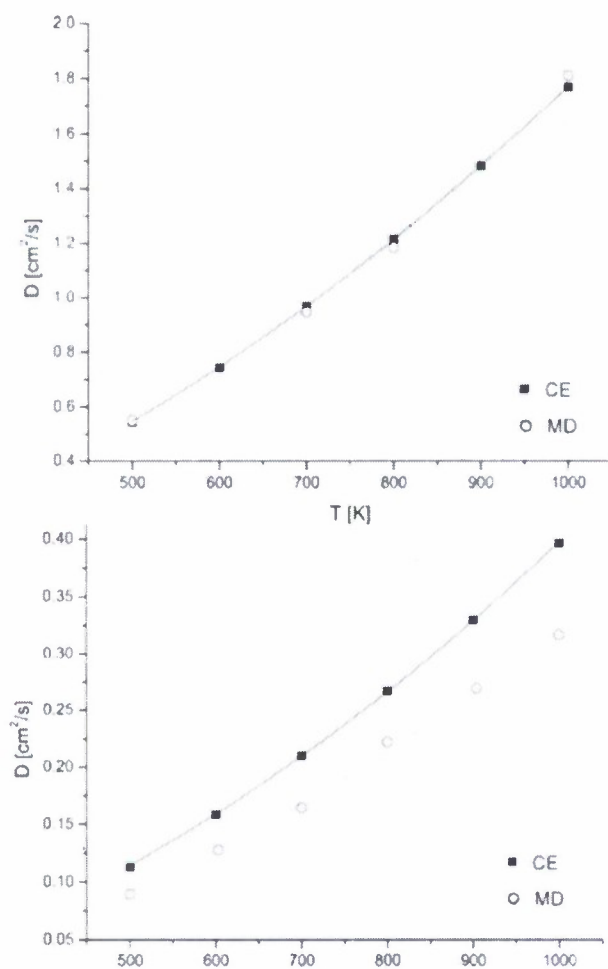

Figure 4:   Binary mass diffusivities of CH4 (upper panel) and C16H34 in nitrogen as function of temperature. CE: Chapman-Enskog; MD: Molecular Dynamics.

Figure 4 shows the comparison between the binary mass diffusivities of methane and hexadecane in nitrogen obtained using the C-E equation and MD simulations. While the agreement with the smallest molecule (almost a spherical one) is very good, the comparison for the

hexadecane/nitrogen mixture (long chain structure) shows a large deviation reaching 17.3 % at high temperatures.

The table below shows the relative deviations between the diffusion coefficients obtained using C-E and MD for the series of alkane C1-C16. For mixtures composed of hydrocarbons in the range C1-C6 the deviation is less than 5%. The MD results consistently show lower diffusivities than those obtained using the C-E equation due to the anisotropic force field interactions.

C_2H_6/N_2	$8.627 \times 10^{-6} T^{1.714}$
C_3H_8/N_2	$6.479 \times 10^{-6} T^{1.725}$
C_4H_{10}/N_2	$5.189 \times 10^{-6} T^{1.735}$
C_5H_{12}/N_2	$4.361 \times 10^{-6} T^{1.743}$
C_6H_{14}/N_2	$3.449 \times 10^{-6} T^{1.750}$
C_7H_{16}/N_2	$3.059 \times 10^{-6} T^{1.757}$
C_8H_{18}/N_2	$2.706 \times 10^{-6} T^{1.764}$
$C_{10}H_{22}/N_2$	$2.124 \times 10^{-6} T^{1.775}$
$C_{12}H_{26}/N_2$	$1.740 \times 10^{-6} T^{1.784}$
$C_{14}H_{30}/N_2$	$1.493 \times 10^{-6} T^{1.792}$
$C_{16}H_{34}/N_2$	$1.309 \times 10^{-6} T^{1.796}$

Table 3. Binary mass diffusion coefficients of n-alkanes in nitrogen as a function of temperature [K] at 1 atm.

4. Integration of the various projects

Results from the projects listed above have been implemented in an initial version of a kinetic mechanism for JP8 surrogate components (JetSurf). The model is being developed through a multi-university research collaboration involving experimental and modeling groups at the University of Southern California, Stanford University, NIST, Drexel University, Princeton University and the Imperial College, London.

PERSONNELL SUPPORTED

Angela Violi, PI (one-summer month salary)
Kyungchan Chae (graduate student)
Steve Fiedler (postdoc)

AFOSR SPONSORED PUBLICATIONS AND PRESENTATIONS:

Peer reviewed Publications:

1. K. Chae, A. Violi "Molecular Dynamics Calculations of the Binary Diffusion Coefficients of Heptane Isomers in Nitrogen", Journal of Chemical Physics, under review (2009).
2. L. K. Huynh,K. Barriger,A. Violi "Kinetics Study of the OH + Alkene = H2O+ Alkenyl Reaction Class", Journal of Physical Chemistry A. 112(7): 1436-1444 (2008).
3. L. Hyunh, A. Violi "Thermal decomposition of methyl butanoate: Ab initio study of a biodiesel fuel surrogate" Journal of Organic Chemistry 73 (1): 94-101 (2008).
4. S.L. Fiedler, S. Izvekov, A. Violi "The effect of temperature on nanoparticle clustering", CARBON 45: 1786-1794 (2007).
5. K. Chae, A. Violi "Thermal Decomposition of Decalin: an ab initio Study" *Journal of Organic Chemistry* 71(22): 8365-8371 (2007).

Conference Proceedings

6. K. Chae, A. Violi "Binary mass diffusion coefficients of polyatomic gases - investigation on the effects of alkane chain length on mass diffusivity", 6th US National Meeting of the Combustion Institute, Ann Arbor, MI, 17-21 May 2009.
7. K. Lin, J. Lai, A. Violi "Insights on the effects of fuel composition on reaction pathways", 6th US National Meeting of the Combustion Institute, Ann Arbor, MI, 17-21 May 2009.

Presentations and Abstracts

1. L.K. Hyunh, K.C. Lin, N. Burtch, A. Violi "Break-down kinetic models of biodiesel surrogates: importance of double bond", 2008 International Combustion Symposium, Montreal, Canada, August 3-8 2008.
2. K. Chae, A. Violi "Calculation of High-Temperature diffusion coefficients for hydrocarbon fuels", 2008 International Combustion Symposium, Montreal, Canada, August 3-8 2008.
3. L.H. Hyunh, A. Violi "Ab Initio Study on the Methyl Butanoate Decomposition" 2007 AIChE Annual Meeting, Salt Lake City, Utah, November 4 -9, 2007
4. S.L. Fiedler, A. Violi "Modeling Temperature Effects on Soot Formation" 2007 AIChE Annual Meeting, Salt Lake City, Utah, November 4 -9, 2007
5. K. Chae, A. Violi "Thermal Decomposition of Decalin: An Ab Initio Study" 2007 AIChE Annual Meeting, Salt Lake City, Utah, November 4 -9, 2007
6. L.H. Hyunh, A. Violi "Theoretical Study on the Methyl Butanoate Decomposition" 30th Meeting of the Italian Section of The Combustion Institute, Ischia, Italy, June 20-23 2007.

EXTRAMURAL-INTRAMURAL INTERACTIONS

During the reporting period, the PI had meetings with Dr. Tim Edwards. Discussions ranged from experiments to modeling of jet fuel surrogate combustion. The PI also interacted with Dr. S. Williams to discuss recent advancements for the JP8 surrogate project.

REFERENCES

1. Tully, F.P., *Hydrogen-atom abstraction from alkenes by OH. Ethene and 1-butene*. Chem. Phys. Lett., 1988. **143**: p. 510-514.
2. Baulch, D.L.C., C.J.; Cox, R.A.; Esser, C.; Frank, P.; Just, Th.; Kerr, J.A.; Pilling, M.J.; Troe, J.; Walker, R.W.; Warnatz, J., *Evaluated kinetic data for combustion modelling*. J. Phys. Chem. Ref. Data, 1992. **21**: p. 411-429.
3. Westbrook, C.K.T., M.M.; Pitz, W.J.; Malte, P.C., *A kinetic study of ethylene oxidation in a well-stirred reactor*. Symp. Int. Combust. Proc., 1988. **22**: p. 863-871.
4. Liu, A., W.A. Mulac, and C.D. Jonah, J. Phys. Chem., 1988. **92**: p. 3828.
5. Liu, G., et al., *Theoretical study on mechanisms of the high-temperature reactions C2H3+H2O and C2H4+OH*. Phys. Chem. Chem. Phys., 2002. **4**: p. 1021 - 1027.
6. Senosiain, J.P., S.J. Klippenstein, and J.A. Miller, *Reaction of Ethylene with Hydroxyl Radicals: A Theoretial Study*. J. Phys. Chem. A, 2006. **110**: p. 6960-6970.
7. Evans, M.G. and M. Polanyi, Proc. R. Soc., 1936. **154**: p. 133.
8. Evans, M.G. and M. Polanyi, Trans. Faraday Soc., 1936. **32**: p. 1333.
9. Polanyi, J.C., *Concepts in reaction dynamics*. Acc. Chem. Res., 1972. **5**(5): p. 161-8.
10. Chapman, S. and T.G. Cowling, *The Mathematical Theory of Non-uniform Gases*. 1970: Cambridge University Press.
11. Erpenbeck, J.J. and W.W. Wood, *Self-diffusion coefficient for the hard sphere fluid*. Physical Review A, 1991. **43**(8): p. 4254 - 4261.
12. Reid, R.C., J.M. Prausnitz, and T.K. Sherwood, *The properties of gases and liquids*. 1987, New York: McGrawHill.
13. Ruckenstein, E. and H. Liu, *Self-Diffusion in Gases and Liquids*. Ind. Eng. Chem. Res., 1997. **36**(9): p. 3927 - 3936.
14. Kubo, R., J. Phys. Soc. Jpn., 1957. **12**: p. 570.
15. Zhou, Y. and G.H. Miller, *Green-Kubo Formulas for Mutual Diffusion Coefficients in Multicomponenet Systems*. J. Phys. Chem, 1996. **100**(13): p. 5516 - 5524.
16. Zhou, Y. and G.H. Miller, *Mutual diffusion in binary Ar-Kr mixtures and empirical diffusion models*. Physical Review E, 1996. **53**(2): p. 1587 - 1601.